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One-pot preparation of novel asymmetric structure nanoparticles and its application in catalysis†

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One-pot method has been applied to the synthesis of new Janus structure nanorods, in which Au nanoparticles are located at one end of mesoporous silica rods. Janus nanorods are synthesized directly by the chloroauric acid solution, without prior preparation of gold or silica nanoparticles. This method is easy and cost-effective for high yield preparation of Janus nanoparticles catalyst. Meanwhile, new Janus nanoparticles have high catalytic activity. Therefore, these new nanoparticles will have broad prospects in catalysis, drug delivery, self-propelled nanodevices, *etc.*

Nanoparticles with asymmetric structure or Janus nanoparticles have wide potential applications in the fields of drug delivery,[1] imaging nanoprobes[2] and self-motile colloidal materials[3] due to their unique structure. This asymmetric structure or "Janus" nanoparticles are usually a combination of two different materials, which simultaneously maintain their own performance between components, which implies that these parts could be modified by different functional groups for further applications.[4] Therefore, the synthesis and application of asymmetric nanoparticles have been considerably developed in recent years.

Various methods are used to synthesize asymmetric particles such as chemical modification,[5] polymerization-induced phase separation method,[6] controlled assembly of materials in microfluidics,[7] metal printing after carrier assembly,[8] *etc.*[9] The methods described above can be summarized into two ideas; one is attaching or growing particles on the pre-synthesized nanoparticles with a special modification.[10] The other is connecting two different particles by a functional group.[11] These methods are usually complex and expensive, and thus the large-scale asymmetric structure synthesis by a cheap and easy route is still a challenge.

Gold nanoparticles have been widely investigated because of their excellent catalytic performance in recent years.[12] Mesoporous silica was often used to solve the aggregation of gold nanoparticles.[13] Another reason is that the abundant silanol groups on silica surfaces made them easier to organic functional, and grafting through different modification methods.[14] However, multiple-step reactions increase the difficulty and cost for the preparation of gold nanoparticles and mesoporous silica nanocomposites. Thus, it is necessary to develop a simple route to obtain solid catalyst carrier similar to mesoporous silica loaded with uniform gold nanoparticles.

In this report, we prepared asymmetric structure nanoparticles with a gold nanoparticle head and mesoporous silica rod body by a simple one-pot method. By studying the formation of asymmetric Janus nanorods, it was disclosed that the spherical micelles of CTAB wrapped chloroauric acid ($HAuCl_4$) formed in the solution first, and then silica rod grew from the micelles. This unique one-dimensional growth results to the formation of an asymmetric structure. The $HAuCl_4$ transferred into gold nanoparticles and mesoporous silica formed (denoted as Janus Au–$mSiO_2$) by calcination at 500 °C. The prepared Janus Au–$mSiO_2$ nanoparticles showed good catalytic properties for the reduction of 4-nitrophenol (4-NP) because of their small size and good dispersibility of the Au nanoparticles. This simple one-pot method for the syntheses and applications of new asymmetric structure nanoparticles (*e.g.* Janus Au–$mSiO_2$) expand in a new direction.

As illustrated in Fig. 1, 50 mg cetyltrimethyl-ammonium bromide (CTAB) was dissolved in water (10 ml) under sonication for 50 min to form rod-like micelles.[15] After that, different amounts of $HAuCl_4$ (0.01 M) were quickly added and 0.5 ml ammonia ($NH_3 \cdot H_2O$) was subsequently added under vigorous stirring, it was noted that the temperature of the mixture was

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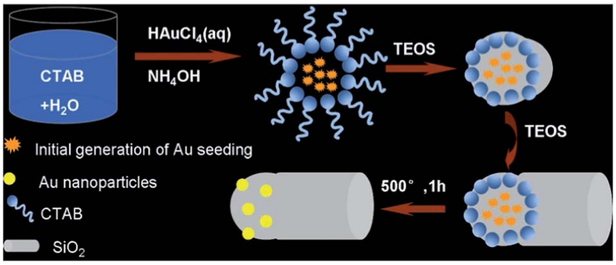

Fig. 1 Schematic diagram of Janus Au–mSiO$_2$ nanoparticles growth.

maintained at 40 °C, and then 30 μL tetraethoxysilane (TEOS) was slowly added into the solution under gentle stirring. The mixture solution was allowed to react 30 min, the as-prepared nanoparticles were washed with ethanol 5 times *via* centrifugation (6000 rpm) and dried at 60 °C. Finally, the Janus Au–mSiO$_2$ nanoparticles were obtained by calcining at 500 °C for 1 h.

Transmission electron microscopy (TEM) images of Janus Au–mSiO$_2$ nanoparticles are shown in Fig. 2A and B. After calcination at 500 °C, HAuCl$_4$ thermally decomposed and formed gold nanoparticles at one end of the silica rods. Most of the silica rod heads contained several Au nanoparticles, which were well dispersed with a size distribution in the range of 2–10 nm. Scanning electron microscopy (SEM) images, as shown in Fig. 2C and D, further confirmed this Janus structure. The Au nanoparticles could be observed in the SEM images, indicating the Au nanoparticles located on the surface of silica rods or Au nanoparticles covered by an ultra-thin layer of silica; however, Au nanoparticles were hardly observed by SEM if they were embedded in the silica rods. This unique structure was advantageous for further modification of different components and will benefit the Au nanoparticles that are directly in contact with the reactant during the catalytic reaction.[23]

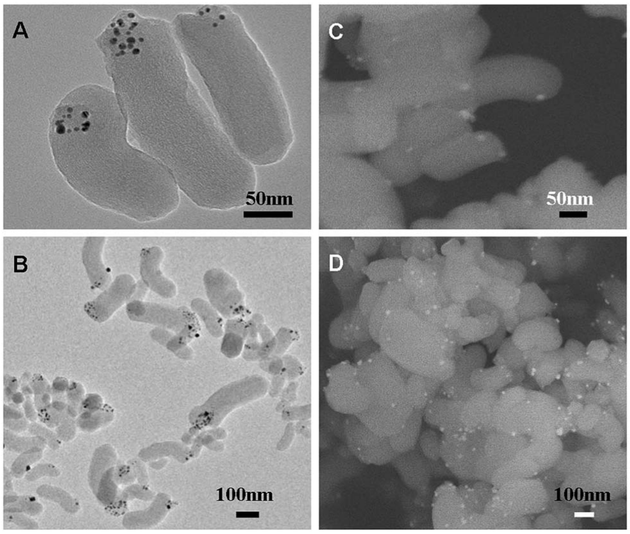

Fig. 2 TEM images (A and B) and SEM images (C and D) of Janus Au–mSiO$_2$ nanoparticles.

To understand the formation of one-pot synthesis of asymmetric Janus Au–mSiO$_2$ nanoparticles, samples were obtained at different reaction time for TEM. In this work, the growth of silica nanorods used the MCM-41 synthesis method, with CTAB working as the pore-forming agent. As shown in Fig. 3A, after sequentially adding HAuCl$_4$ and $NH_3 \cdot H_2O$ into the CTAB solution, spherical micelles containing HAuCl$_4$ were formed in the solution. High energy electron beam in the TEM instrument may directly reduce $AuCl_4^-$ into Au nanoparticles. This was the reason for the aggregation of gold nanoparticles within small circles in Fig. 3A. After adding TEOS, the spherical micelles were not destroyed, and silica aggregates anchored to the surface of the micelles, as shown Fig. 3B. As the reaction proceeded, the silica grew into a quasi-sphere along the surface of microemulsion bounded CTAB micelles (Fig. 3C). Then, the mesosilica nanorods developed due to the presence of CTAB in the solution, as shown in Fig. 3D and S1A,† which was similar to our previous report.[15]

The Janus Au–mSiO$_2$ can be well-redispersed into water. The optical properties of the Janus Au–mSiO$_2$ nanoparticles in aqueous solutions were performed by UV-vis spectroscopy, as shown in Fig. S2.† The image in the lower left corner is the asymmetric Janus Au–mSiO$_2$ nanoparticles before annealing; the particle colour was yellow and no UV absorption peaks of the gold nanoparticles around 520 nm was observed, indicating that the HAuCl$_4$ was not reduced. After thermal treatment, the nanoparticles powder showed a reddish brown color, as shown in the inset image in the right corner. An adsorption peak appeared at 527 nm in the UV-vis spectrum, indicating the formation of gold nanoparticles. This confirmed that $AuCl_4^-$ could be reduced to form gold nanoparticles by high temperature treatment.[16] With the addition of different amounts of HAuCl$_4$ the adsorption peak shifted from 527 nm to 540 nm, which indicated that the size of gold nanoparticles became larger or aggregated.[17] The possible reason was that with an increase in added amounts of HAuCl$_4$, gold ion density of per unit volume increased resulting in the change of nanoparticles after annealing.

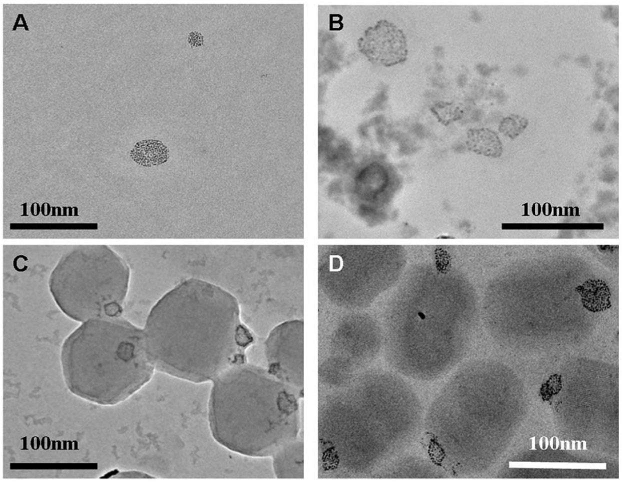

Fig. 3 Time-resolved TEM images of the growth process of Janus Au–mSiO$_2$ nanoparticles.

After high temperature treatment, the silica rods possessed mesoporous structure in Janus Au–mSiO$_2$ due to existing CTAB, which was potentially useful and important for drug or dye delivery.[18] High resolution TEM images (Fig. S1B†) discloses the nanostripe structure. Furthermore, the characterization of the mesoporous structure was evaluated by N$_2$ adsorption/desorption isotherms and X-ray diffraction (XRD) measurements. N$_2$ adsorption/desorption isotherms of SiO$_2$ was carried out at 77 K. Fig. S3(a)† exhibited type IV BET isotherms for SiO$_2$, which is a signature feature of mesoporous materials.[19] The BET surface area and the BJH adsorption cumulative volume of pores of the mesoporous silica particles were as high as 1090.3 m^2 g^{-1} and 0.73 cm^3 g^{-1}, which were advantageous for drug delivery applications and complete use of the catalyst in chemical reactions. When subjected to XRD patterns analysis, we used Janus Au–mSiO$_2$ nanoparticles obtained by adding 1 ml HAuCl$_4$. As shown in Fig. S3(b),† the small-angle XRD patterns of mesoporous SiO$_2$ and Janus Au–mSiO$_2$ exhibited similar diffraction pattern at 0.8°, which confirmed that Janus Au–mSiO$_2$ has a similar structure as mesoporous SiO$_2$. In addition, gold nanoparticles formed by HAuCl$_4$ did not destroy the characteristic structure of mesoporous silica. Fig. S3(c)† showed the wide-angle XRD patterns of mesoporous SiO$_2$ and Janus Au–mSiO$_2$, the peaks at 38°, 44°and 64° corresponding to the (111), (200), (220) crystal faces of Au nanoparticles.[20] No diffraction peaks from any other impurities were detected. The average particle size calculated from the Au (111) peak according to the Scherrer's formula was 7.3 nm,[21] which was in good agreement with the TEM results.

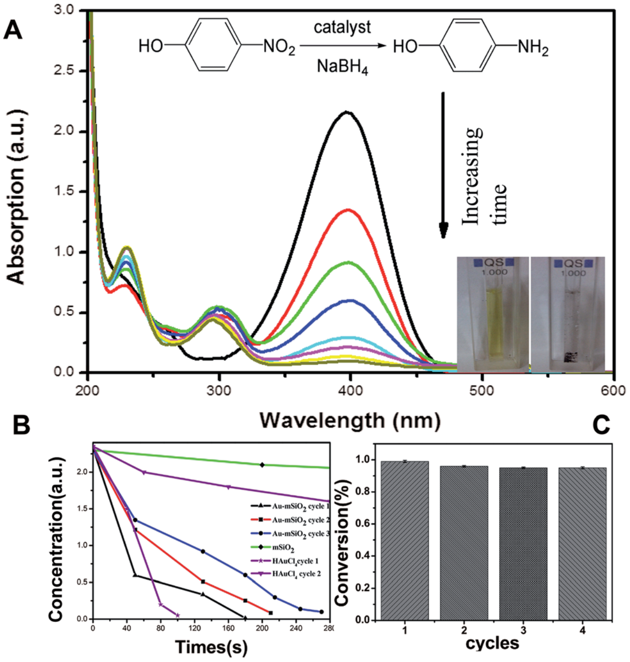

Fig. 4 Successive UV-vis absorption spectra of the reduction of 4-nitrophenol by NaBH4 in the presence of Janus Au–mSiO$_2$ (A) and (B) the relationship between 4-nitrophenol concentration (a.u.) with reaction time (s) (C) the reusability of Au–mSiO$_2$ as a catalyst for the reduction of 4-nitrophenol.

As we know, Au nanoparticles were good catalysts for the catalytic reduction reaction. Here, we selected this reaction as a model system to evaluate the catalytic effect of gold nanoparticles in Janus Au–mSiO$_2$. 4-Nitrophenol (4-NP) are often used in pesticides, herbicides, water pollution and its control is also a significant public concern.[22] Nevertheless, 4-aminophenol (4-AP) produced by sodium borohydride (NaBH$_4$) reduction of 4-NP has broad industrial applications in photographic development, corrosion inhibition, as lubricants and others. In addition, the reaction could be easily monitored by UV-visible absorption spectroscopy. First, 2 mg of Janus Au–mSiO$_2$ nanoparticles were added to 0.8 ml 4-NP (0.03 mg ml^{-1}) solution at room temperature, and then 0.2 ml of NaBH$_4$ (0.1 M) solution was added; with UV spectra detecting the change, as shown in Fig. 4A, 4-NP characteristic peak at 400 nm decreased with the increasing time, indicating that the amount of 4-NP decreased. On the contrary, the peak at 225 nm increased with the proceeding reaction. Meanwhile, the color of the reaction solution gradually faded and finally turned fully transparent. As shown in Fig. 4B, the three reactions finished within 180 seconds, 215 seconds and 270 seconds, respectively. Time possibly increased because of the loss of the catalyst in the recycling. When the mesoporous SiO$_2$ nanorods (15 mg ml^{-1}) without loaded Au nanoparticles was added into the reaction, it took about 24 h before the reaction solution became fully clear from yellow. These results indicate that the Janus Au–mSiO$_2$ has good catalytic properties for catalytic reduction. When only 0.2 ml HAuCl$_4$ is added, the catalytic reaction speed was 100 seconds for the first time, but when used again, the catalytic effect decreased significantly. The reason is that the gold nanoparticles obtained by the reduction of gold ions easily reunite and lose catalytic activity. Moreover, rod-shaped nanostructure even after accumulation between nanoparticles can maintain adequate pores, as shown in Fig. 2D, which will facilitate that the reactants and catalyst remain fully in contact and improve the utilization rate of the catalysts. The Janus Au–mSiO$_2$ can be easily collected by simple centrifugation that was very helpful for the recycling of catalyst. The completion of the catalytic reaction in 4 cycles, as shown in Fig. 4C, in four cycles, respectively, the completion of the reaction reached 99%, 96%, 95% and 95%, the completion of the catalyst in 4 cycles are more than 95%. Thus, the Janus Au–SiO$_2$ nanoparticles had a high catalytic activity for the dispersion of gold particles. This provided the possibility for the controllable catalytic location by the nanoparticles with an asymmetric structure assembling.

Conclusions

A simple one-pot method had been used to synthesize new asymmetric structure nanoparticles with both gold nanoparticles and mesoporous silica rods. Janus Au–mSiO$_2$ nanorods were synthesized directly using the chloroauric acid solution, without the prior preparation of gold or silica nanoparticles. The silica rods of Janus Au–mSiO$_2$ had a uniform scale, gold nanoparticle in the size range of 2–10 nm concentrated at one end of silica rods, and had a good dispersion that gave it good catalytic activity. This method of using chloroauric acid solution and TEOS for a direct assembly of Janus Au–mSiO_2 in aqueous solution was simple, efficient and provided a new direction for exploring the synthesis and applications of new asymmetric nanoparticles.

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Notes and references

1 A. K. Salem, P. C. Searson and K. W. Leong, *Nat. Mater.*, 2003, **2**, 668.
2 (*a*) J. Choi, Y. Zhao, D. Zhang, S. Chien and Y. H. Lo, *Nano Lett.*, 2003, **3**, 995; (*b*) M. Yoshida, K. H. Roh and J. Lahann, *Biomaterials*, 2007, **28**, 2446.
3 J. R. Howse, R. A. L. Jones, A. J. Ryan, T. Gough, R. Vafabakhsh and R. Golestanian, *Phys. Rev. Lett.*, 2007, **99**, 048102.
4 J. L. Tang, K. Schoenwald, D. Potter, D. White and T. Sulchek, *Langmuir*, 2012, **28**, 10033.
5 S. Pradhan, L. P. Xu and S. W. Chen, *Adv. Funct. Mater.*, 2007, **17**, 2385.
6 V. N. Manoharan, M. T. Elsesser and D. J. Pine, *Science*, 2003, **301**, 483.
7 S. Xu, Z. Nie, M. Seo, P. Lewis, E. Kumacheva, H. A. Stone, P. Garstecki, D. B. Weibel, I. Gitlin and G. M. Whitesides, *Angew. Chem.*, 2005, **117**, 734.
8 K. Chaudhary, Q. Chen, J. J. Juárez, *et al.*, *J. Am. Chem. Soc.*, 2012, **31**, 12901.
9 (*a*) Z. He and I. Kretzschmar, *Langmuir*, 2012, **26**, 9915–9919; (*b*) Z. He and I. Kretzschmar, *Langmuir*, 2013, **51**, 15755.
10 (*a*) T. Chen, G. Chen, S. Xing, T. Wu and H. Chen, *Chem. Mater.*, 2010, **22**, 3826; (*b*) T. Tanaka, M. Okayama, Y. Kitayama, Y. Kagawa and M. Okubo, *Langmuir*, 2010, **26**, 7843.
11 (*a*) M. D. McConnell, M. J. Kraeutler, S. Yang and R. J. Composto, *Nano Lett.*, 2010, **10**, 603; (*b*) C. Tang, C. Zhang, J. Liu, X. Qu, J. Li and Z. Yang, *Macromolecules*, 2010, **43**, 5114.
12 (*a*) A. Cros, J. Derrien and F. Salvan, *Surf. Sci.*, 1981, **2**, 471; (*b*) X. Chen, Y. An, D. Zhao, *et al.*, *Langmuir*, 2008, **15**, 8198; (*c*) D. Xiong, Z. Li, L. Zou, *et al.*, *J. Colloid Interface Sci.*, 2010, **2**, 273.
13 L. Chen, J. Hu and R. Richards, *J. Am. Chem. Soc.*, 2008, **3**, 914–915.
14 S. Jana, S. Bhunia, B. Dutta and S. Koner, *Appl. Catal., A*, 2011, **392**, 225.
15 L. Zhang, F. Zhang, W. F. Dong, J. F. Song, Q. S. Huo and H. B. Sun, *Chem. Commun.*, 2011, **47**, 1225.
16 T. Rao, X. H. Dong, B. C. Katzenmeyer, C. Wesdemiotis, S. Z. D. Cheng and M. L. Becker, *Soft Matter*, 2012, **8**, 2965.
17 Y. H. Su, Y. F. Ke, S. L. Cai and Q. Y. Yao, *Light: Sci. Appl.*, 2012, **1**, e14.
18 B. G. Trewyn, S. Giri and I. I. Slowing, *Chem. Commun.*, 2007, 3236.
19 F. Kleitz, S. H. Choi and R. Ryoo, *Chem. Commun.*, 2003, 2136.
20 J. Du, J. Qi, D. Wang and Z. Tang, *Energy Environ. Sci.*, 2012, **5**, 6914.
21 A. L. Patterson, *Phys. Rev.*, 1939, **56**, 978.
22 Z. Zhang, C. Shao, P. Zou, P. Zhang and M. Zhang, *Chem. Commun.*, 2011, **47**, 3906.
23 L. Zhang, F. Zhang, Y. S. Wang, *et al.*, *Soft Matter*, 2011, **7**, 7375.